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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Test/QA Plan for Verification of Portable Analyzers for Detection of Cyanide in Water

TEST/QA PLAN

for

VERIFICATION OF PORTABLE ANALYZERS FOR THE DETECTION OF CYANIDE IN WATER

January 8, 2003

Prepared by

Battelle
505 King Avenue
Columbus, OH 43201-2693

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ETV Advanced Monitoring Systems Center

Test/QA Plan for Verification of Portable Analyzers for Detection of Cyanide in Water

Version 1

January 8, 2003

APPROVAL:

Name _____

Company _____

Date _____

DISTRIBUTION LIST

Elizabeth A. Betz
U.S. Environmental Protection Agency-HEASD
National Exposure Research Laboratory
E205-01 EPA Mailroom
Research Triangle Park, NC 27711

Robert Fuerst
U.S. Environmental Protection Agency-HEASD
National Exposure Research Laboratory
D205-05 EPA Mailroom
Research Triangle Park, NC 27711

Susan Lumpkin
U.S. Environmental Protection Agency-HEASD
National Exposure Research Laboratory
D205-05 USEPA Mailroom
Research Triangle Park, NC 27711

Elizabeth Hunike
Quality Assurance Specialist
U.S. Environmental Protection Agency-HEASD
National Exposure Research Laboratory
D205-03 EPA Mailroom
Research Triangle Park, NC 27711

Jim Eagan
LaMotte Company
802 Washington Ave.
Chestertown, MD 21620

Joanne Carpenter
CHEMetrics
4295 Catlett Road
Calverton, VA 20138

John Murray
WTW Measurement Systems
3170 Metro Parkway
Fort Myers, FL 33916

John Esposito
Orbeco-Hellige
185 Marine St.
Farmingdale, NY 11735

Steve West
Thermo-Orion
500 Cummings Ctr.
Beverly, MA 01915

Karen Riggs
Bruce Alleman
Amy Dindal
Ryan James
Zachary Willenberg
Battelle
505 King Ave.
Columbus, OH 43201

1.0 INTRODUCTION

1.1 Test Description

This test/quality assurance (QA) plan provides procedures for a verification test of portable analysis technologies that determine the free cyanide ion in water, which hereafter will be referred to as "cyanide". The verification test will be conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) program. The purpose of ETV is to provide objective and quality assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about purchasing and applying these technologies.

The verification test will be performed by Battelle, of Columbus, Ohio, which is managing the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with EPA. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil. In performing the verification test, Battelle will follow the procedures specified in this test/QA plan, and will comply with the data quality requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Center" (QMP).[1]

1.2 Test Objective

The verification of portable cyanide analyzers will be conducted to quantify the analytical and operational performance characteristics of these technologies under a specific set of test conditions. A variety of quality control, performance evaluation, drinking, and surface water samples will be analyzed by the participating technologies to assess their ability to measure cyanide. To evaluate the accuracy of the results generated by each technology, each sample will also be analyzed using an accepted reference method, and the reported

concentrations will be compared with the concentrations reported by the portable cyanide analyzer. The precision of the results will be evaluated by making replicate measurements on each sample. Operator bias will be assessed by comparing results generated by a technical and non-technical operator. Qualitative characteristics of each technology such as ease of use and field portability will be assessed by observations made by the test coordinator throughout the verification test. The results from each technology will be reported individually. No direct comparison will be made between technologies, but each technology will undergo identical testing so it is convenient for end users to evaluate the ETV testing results.

1.3 Organization and Responsibility

The verification test will be performed by Battelle with the participation of the interested vendors who will be having their analyzers verified. The testing will occur at Battelle's Columbus, Ohio laboratories and at private residences in the Columbus area. The organizational chart shown in Figure 1 shows the individuals from Battelle, the vendor companies, and the EPA who will have responsibilities in the verification test.

1.3.1 Battelle

Dr. Ryan James is the AMS Center Verification Test Coordinator. In this role, Dr. James will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. More specifically, he will:

- Assemble a team of qualified technical staff to conduct the verification test.
- Direct the team in performing the verification test in accordance with the test/QA plan.

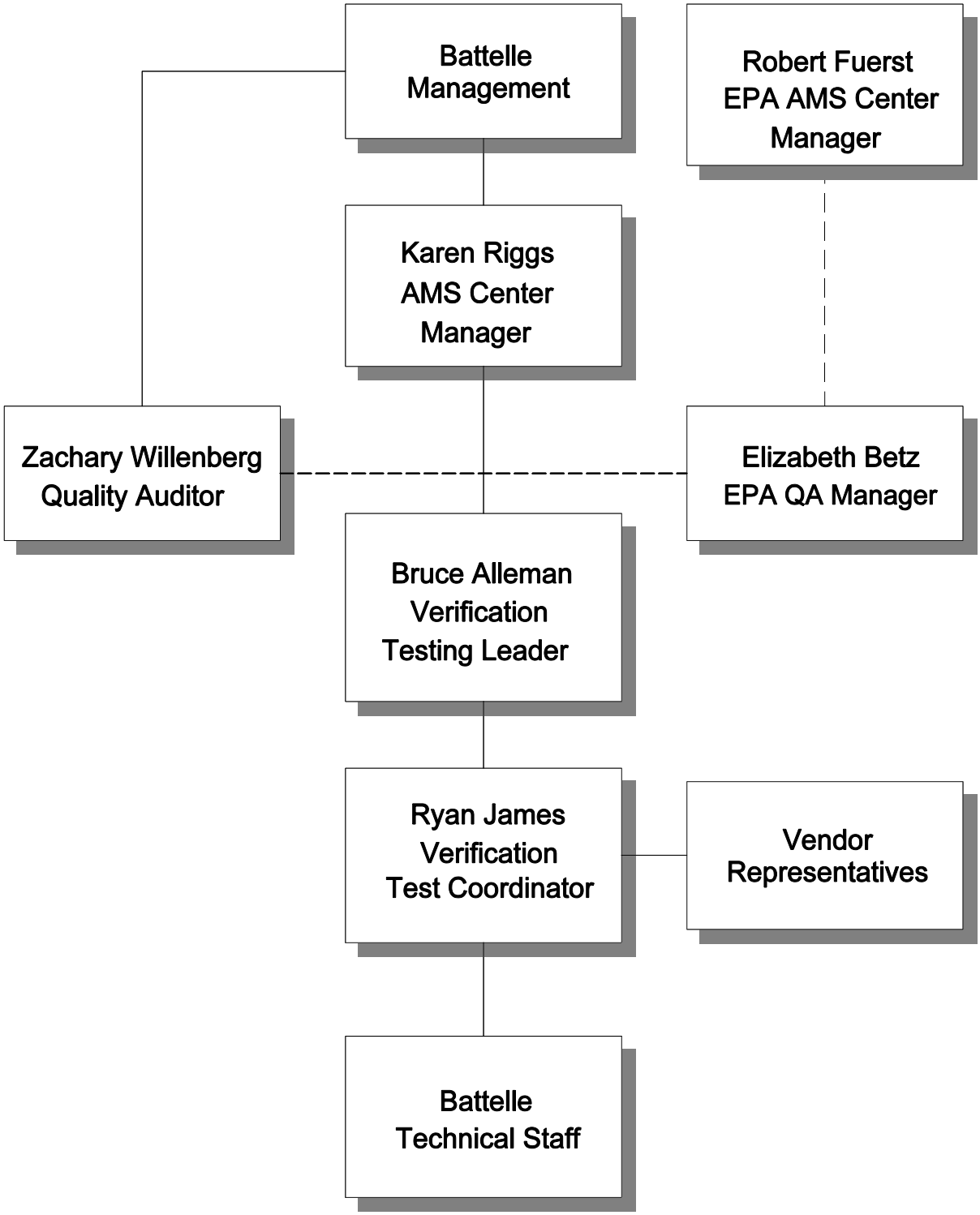

Figure 1. Organization Chart for the Verification Test

- Ensure that all quality procedures specified in the test/QA plan and in the QMP are followed.
- Prepare the draft test/QA plan, verification reports, and verification statements.
- Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments.
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary.
- Serve as the primary point of contact for vendor representatives.
- Establish a budget for the verification test and monitor staff effort to ensure that budget is not exceeded.
- Ensure that confidentiality of vendor information is maintained.

Dr. Bruce C. Alleman is a Verification Testing Leader for the AMS Center. As such, Dr. Alleman will provide technical guidance and oversee the various stages of verification testing. He will:

- Support Dr. James in preparing the test/QA plan and organizing the testing.
- Review the draft test/QA plan.
- Review the draft verification reports and statements.

Ms. Karen Riggs is Battelle's manager for the AMS Center. As such, Ms. Riggs will:

- Review the draft test/QA plan.
- Review the draft verification reports and verification statements.
- Coordinate distribution of the final test/QA plan, verification reports, and verification statements.

- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test.
- Ensure that vendor confidentiality is maintained.
- Support Dr. James in responding to any issues raised in assessment reports and audits.
- Maintain communication with EPA's technical and quality managers.
- Facilitate a stop work order if Battelle or EPA QA staff discovers adverse findings.

Battelle Technical Staff and temporary staff assistance will conduct the testing of the analyzers during the verification test and associated experimental activities. The responsibilities of these technical staff include:

- Assist in the collection of samples.
- Analyze samples for the verification test as described in this test/QA plan.

Mr. Zachary Willenberg is Battelle's Quality Manager for the AMS Center. As such Mr. Willenberg will:

- Review the draft test/QA plan.
- Conduct quality review of reference laboratory documentation (see Section 1.3.4).
- Conduct a technical systems audit once during the verification test.
- Audit at least 10% of the verification data.
- Prepare and distribute an assessment report for each audit.
- Verify implementation of any necessary corrective action.

- Issue a stop work order if self audits indicate that data quality is being compromised; notify Battelle's Center Manager if stop work order is issued.

- Provide a summary of the quality assurance/quality control (QA/QC) activities and results for the verification reports.

- Review the draft verification reports and statements.

- Have an overall responsibility for ensuring that the test/QA plan is followed.

Mr. Gary Carlin is Battelle's Environmental Health and Safety representative for the AMS Center. As such Mr. Carlin will:

- Review the safety issues related to handling cyanide and provide input into the test/QA plan.

- Advise staff working with cyanide on personal protective equipment and training needs.

1.3.2 Vendors

Vendor representatives will:

- Review the draft test/QA plan.

- Approve the test/QA plan.

- Provide two off-the-shelf models of the analyzers to be verified for the duration of the verification test.

- As desired, instruct Battelle personnel on how to operate and maintain the analyzers prior to testing.

- If desired, provide a representative to operate the analyzers during the verification tests

- Review their respective draft verification report and statement.

1.3.3 EPA

EPA's responsibilities in the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality and Management Plan of the Pilot Period (1995-2000)" (QAMP). The roles of the specific EPA staff are as follows:

Ms. Elizabeth Betz is EPA's Quality Assurance Manager. For the verification test, Ms. Betz will:

- Review the draft test/QA plan.
- Direct the performance, at the EPA's discretion, of external technical systems audit(s) during the verification test.
- Notify the EPA AMS Center Manager to facilitate a stop work order if the external audit indicates that data quality is being compromised.
- Prepare and distribute an assessment report summarizing results of the external audit.
- Review draft verification reports and statements.

Mr. Robert Fuerst is EPA's manager for the AMS Center. As such, Mr. Fuerst will:

- Review the draft test/QA plan.
- Approve the final test/QA plan.
- Notify the Battelle Center Manager to facilitate a stop work order if the external audit indicates that data quality is being compromised.
- Review the draft verification statements.
- Review the final verification reports.

1.3.4 Commercial Laboratory

Battelle will collaborate with a commercial laboratory that will:

- Perform reference analyses of all test and QA samples of unknown concentrations.
- Submit to Battelle the results of the reference analyses in an agreed upon format.

In order to be selected to perform the reference analyses during the verification test, a commercial laboratory will need to demonstrate its competence to perform the needed cyanide analysis (see Section 2.4) by providing Battelle with copies of: their method/standard operating procedure, quality assurance manual, state government certifications/approvals for cyanide analysis, and staff training records, where available. Additionally, Battelle will prepare and submit several samples of potassium cyanide to the laboratory. Battelle will prepare these samples at concentrations unknown to the prospective laboratory. The commercial laboratory's reported concentrations of the submitted quality control standards will need to be within 25% of their known concentrations. If the prospective laboratory does not comply fully with each of the above requirements, another laboratory will be selected and their competence verified in a similar manner.

2.0 VERIFICATION APPROACH

2.1 Scope of Testing

Cyanide is present in various forms in water. This verification test focuses on the detection of the free cyanide ion (CN^-) which in this document is referred to as "cyanide". At high doses, this form of cyanide inhibits cellular respiration and in some cases can result in death. In drinking and surface water under ambient conditions, cyanide evolves from aqueous hydrogen cyanide, sodium cyanide, potassium cyanide, and other ionic complexes where cyanide is released easily when dissolved in water. Because of the toxicity of cyanide to humans, the EPA has set 0.2 mg/L as the maximum concentration of cyanide that can be present in drinking water. The reference method to be used during this verification test is EPA Method 335.1 "Cyanides Amenable to Chlorination". This method was selected because it measures the concentration of the cyanide ion in water samples under ambient conditions, which is the same form of cyanide that the technologies to be verified are designed to measure.

This test/QA plan specifically addresses verification testing of 1) portable test kits, and 2) ion selective electrodes that provide quantitative measurements of cyanide in water. The test kits consist of a portable colorimeter that requires a specific reagent solution. Typically the reagent and the water sample are mixed, and the mixture is inserted into the colorimeter and probed photometrically to provide a quantitative determination of cyanide. These analyzers report results via a digital display or electronic output signal. The cyanide ion selective electrodes work as sensors. A membrane at the end of an electrode allows only the negatively charged cyanide ion to be transported through, thus creating a potential difference across that membrane. This potential difference is directly proportional to the concentration of free cyanide ions in the bulk solution. Upon calibration in solutions of cyanide, the electrode is placed in a water sample and the concentration of free cyanide in the water is reported through a digital output.

The verification of all the portable cyanide analyzers will be done through the analysis of prepared, surface water, and drinking water samples by both the analyzers being verified and by a standard reference method. Statistical comparisons of the analytical results from the reference method and the analyzers being verified will provide a basis for quantitative performance evaluations of the analyzers. Each of the analyzers will also be evaluated in terms of ease of use and sample throughput.

The potable cyanide analyzers provide a measure of the analyte concentration, and will be evaluated in terms of:

- accuracy
- precision
- linearity
- method detection limit
- inter-unit reproducibility
- matrix effects
- response of analyzer at cyanide concentrations dangerous to human health
- operator bias (test kit analyzers only)
- portability
- ease of use.

2.2 Experimental Design

Two units of each portable cyanide analyzer being tested will undergo verification testing. The verification results for the two units will be reported and intercompared to assess unit-to-unit reproducibility. The verification test will involve challenging the analyzers being verified with a variety of test samples, including sets of drinking and surface water samples representative of those likely to be analyzed using these devices. All samples will be analyzed by the technologies being verified and by a standard reference method. Comparison of the

results from the analyzers to those from the reference method will be used to quantitatively assess accuracy, linearity, and detection limit. Multiple aliquots of each test sample will be analyzed separately to assess precision of both the analyzers being verified and the reference method.

The test kit analyzers are designed for use by non-technical operators while the ion selective electrodes are not. Therefore each test kit analyzer will be tested independently by two separate operators (technical and non-technical) to test for the existence of operator bias on analyzer performance. The vendor will have the option of providing a representative to serve as the technical operator or of training Battelle staff to serve as the technical operator. The non-technical staff member will have little prior knowledge of the analyzer being verified and will have little or no previous laboratory experience. Both operators will analyze all of the test samples. Each operator will manipulate the water samples and reagents to generate a solution that can be probed photometrically. Then, each operator will analyze that solution using both units of a given vendor's analyzer. More than one technical and/or non-technical operators may be used by Battelle. The operators will be uniquely identified in the verification report so it is clear what operator produced what data.

Matrix effects will be assessed by separately evaluating accuracy, precision, and linearity on distinctly different sample matrices, such as samples prepared in pure water with varying cyanide concentrations and drinking and surface water samples both spiked with cyanide and left unspiked. Sample throughput will be estimated based on the time required to analyze a sample set. Performance parameters, such as ease of use and reliability, will be based on documented observations of the operators and test coordinator. Each analyzer will be used in a field environment, as well as in a laboratory setting, to assess the impact of field conditions on performance.

2.3 Test Samples

Test samples to be used in this verification test will include quality control (QC) samples, performance test (PT) samples, and drinking and surface water samples. Tables listing the number and type of different samples to be analyzed using each type of analyzer are provided in Appendix A. The QC and PT samples will be prepared from purchased standards. The QC sample concentrations will be targeted to the EPA maximum contaminant level (MCL) in drinking water which for cyanide is 0.2 mg/L. The PT samples will cover the range from 0.03 mg/L to 0.8 mg/L for the test kit analyzers. The performance of the test kit analyzers will also be evaluated with three samples at concentrations that could be lethal if a volume the size of a typical glass of water was ingested. The ion selective electrode analyzers will be tested with PT samples ranging from 0.03 mg/L to 25 mg/L, but will not be subjected to the lethal/near-lethal concentrations. In order to evaluate the field portability of these analyzers, some of the drinking water samples indicated in Appendix A will be analyzed in a field setting. Other drinking and surface water samples will be shipped to Battelle and analyzed blindly by the vendors' analyzers in a laboratory setting. All the samples will be analyzed by each of the two units of each analyzer undergoing testing and by a standard reference method.

2.3.1 QC Samples

Prepared QC samples will include both laboratory reagent blanks (RB) and laboratory fortified matrix (LFM) samples. The RB samples will be prepared from ASTM type II deionized water and will be exposed to identical handling and analysis procedures as other prepared samples, including the addition of all reagents. These samples will be used to help ensure that no sources of contamination are introduced in the sample handling and analysis procedures. The LFM samples will be prepared as aliquots of drinking and surface water samples spiked with KCN to increase the analyte concentration by 0.2 mg/L. In the case of the drinking water

samples to be analyzed in the field, the spike solution used to prepare the LFM will be prepared in the laboratory and brought to the field site. For the rest of the samples, the LFM will be prepared similarly, only within a Battelle laboratory, not in a field setting. Since no cyanide is expected to be detectable in the drinking and surface water samples, four LFM samples will be analyzed for each source of water. These samples will be used to help identify if matrix effects have an influence on the analytical results.

Quality control standards (QCS) will be used to ensure the proper calibration of the ion selective electrodes (ISE) being verified and of the reference instrument. The instruments in the colorimetric test kits are factory calibrated so no additional calibration can be performed by the operators. However, QCS will still be analyzed (without defined performance limits) by the colorimeters to demonstrate their proper functioning to the operator. The QCS standards will be purchased from a commercial supplier and subject only to dilution as appropriate. A QCS (as part of the reference laboratory's SOP) will be analyzed before and after the testing period, as well as after every tenth sample. The reference method will be required to measure the concentrations of the QCS to within 25% of the known concentration. If the difference is larger that 25%, the data collected since the most recent QCS will be flagged and proper maintenance will be performed to regain accurate cyanide measurement, according to the reference laboratory's protocols. For the ISE technologies, if there is a greater than 25% decrease in the accuracy of the QCS, the operator will polish the electrode and re-calibrate in attempt to improve the accuracy of the measurement. Additional standards will also be purchased from an independent supplier, for use in a performance evaluation audit, as described in Section 6.2.1.

2.3.2 Performance Test (PT) Samples

The PT samples will be prepared in the laboratory using ASTM Type II deionized water as the water source and will include only cyanide at various concentrations. These samples will be used specifically to help determine the analyzer accuracy, linearity, and detection limit. To

determine the detection limit of the analyzers, a solution with a concentration five times the vendor's reported detection limit will be used. Seven nonconsecutive replicate analyses of this solution will be made to obtain precision data with which to determine the method detection limit. Additionally, solutions will be prepared to assess the linearity over a broad concentration range. Four aliquots of each of these solutions will be analyzed separately to assess the precision of the analyzers. The concentrations of the PT samples are listed in the tables within Appendix A. The operators will analyze the PT samples blindly in a random order to minimize any bias that could occur.

Because cyanide is particularly toxic, ETV stakeholders and other end users of these analyzers are interested in the response of these analyzers when the cyanide is present in drinking water at lethal and near-lethal concentrations (>50 mg/L). To address this issue, three test samples, prepared in ASTM water, at lethal or near-lethal concentrations (50, 100, and 250 mg/L) will be analyzed. While typically the analyzers are not designed to quantitatively measure these extreme concentrations, the operators and test coordinator will make qualitative observations of their operation while analyzing such samples. Observations of unusual operational characteristics (rate of color change, unusually intense color, unique digital readout, etc.) will be documented and reported so the end user can be made aware of what analyzer performance characteristics may serve as indicators of lethal or near-lethal concentrations. The ion selective electrode analyzers will be exempted from the testing of lethal and near-lethal concentrations because the electrode membrane is damaged when placed in concentrations of cyanide greater than 30 mg/L.

2.3.3 Drinking and Surface Water Samples

Water samples, including tap water (well and local distribution sources) and fresh surface water will be collected from a variety of sources and will be used to evaluate technology performance. Samples will be collected from the following sources:

- Residential tap (Columbus water)
- Residential tap (well water)
- Alum Creek Reservoir
- Olentangy River
- Entry of water distribution centers (post-treatment) from five cities, one city each from the Northwestern, Southwestern, Midwestern, Southeastern, and Northeastern region of the U.S.

In general, approximately 8-L water samples will be collected as part of this verification test. The water samples will not be characterized in any way (i.e., hardness, alkalinity, etc.) other than for cyanide concentration. They will be split into two 4-L sub-samples. One sub-sample will be spiked with 0.2 mg/L cyanide, to provide LFM aliquots, and the other sub-sample will remain unspiked. Four 400-mL aliquots to be used for analysis by the vendors' test kit analyzers (~10 mL per replicate analysis) and ion selective electrodes (~100 mL total needed) will be taken from each sub-sample. Also taken from each sub-sample will be four 500-mL aliquots that will be used for analysis by the reference method. Cyanide is not expected to be detectable in any of the drinking or surface water samples analyzed during this test. In order to avoid replicating non-detectable concentrations, only one unspiked aliquot of each source of water will be analyzed if cyanide is not detectable in the first aliquot analyzed by each participating technology. If there is detectable cyanide in that initial aliquot, three additional aliquots of that sample will be analyzed in addition to four LFM aliquots. Four LFM aliquots will be prepared and analyzed for every drinking and surface water source, regardless of the concentration of the initial aliquot. Each aliquot analyzed by the analyzers being verified will also be analyzed by the reference method.

Some of the verification test samples will be collected and then shipped to Battelle to undergo verification testing in a Battelle laboratory. These include surface water from the

Olentangy River and Alum Creek Reservoir and drinking water samples collected at five cities located in five different regions of the U.S. The surface water will be collected near the shoreline by submerging the containers no more than one inch below the surface of the water. Representatives of each city's water treatment facility will provide Battelle a sample of water that has completed the water treatment process, but has not yet entered into the water distribution system. These samples will be preserved with NaOH at a pH of greater than 12 and the samples will be analyzed within 14 days. Once the samples arrive at Battelle, they will be split into unspiked background and LFM sub-samples as described above, and analyzed by the participating technologies.

Testing the operation of the analyzers in a field setting is a key component of the verification test. Finding out the performance of each analyzer while being used outside the laboratory under outdoor conditions and without the availability of miscellaneous laboratory supplies is important to the stakeholders and end users of these analyzers. The residential tap water (both well and Columbus water) samples will be used to verify the field portability of these analyzers. The residential tap water samples will be analyzed three different ways to verify each technology's performance. Twenty-four liters of water will be collected from an outside spigot at the participating residences and split into three approximately 8-L samples. The first sample will be analyzed outdoors at the residence under the current weather conditions (meteorological conditions at the time of field sampling and analysis will be documented), the second sample will be brought inside the residence and allowed to equilibrate to room temperature before testing, and the third sample will be transported back to Battelle for testing in the laboratory like the samples collected elsewhere and shipped to Battelle. Each 8-L sample will be split and analyzed as described in the second paragraph of this section. If any of the samples are not able to be analyzed within 24 hours of sampling, they will be preserved with NaOH to a pH greater than 12 at 4EC.

2.4 Reference Method

Technology verification will involve, in part, comparison of the results from each analyzer being verified to the results obtained from an appropriate reference method. The reference method chosen for this verification test, for both the ion selective electrodes and test kit technologies, is an EPA standard method for the analysis of water. Samples will be analyzed using visible spectroscopy according to EPA Method 335.1[2], Cyanides, Amenable to Chlorination. This method incorporates two determinations of total cyanide. One determination is done after the free cyanide in the sample has been chlorinated to CNCl, which degrades quickly, and the second is done without chlorination. The concentration of free cyanide is given by the difference of the two measurements of total cyanide.

3.0 MATERIALS AND EQUIPMENT

In general, this verification test relies on the materials and equipment provided by the vendors. Battelle will provide the following equipment and materials.

3.1 Laboratory Supplies

The following laboratory supplies will be needed for the preparation of the PT samples and the QC samples:

- ASTM type II water
- 4-L, 1-L, 250-mL, and 100-mL Class A volumetric flask
- 10-mL Class A volumetric pipets
- 10-mL and 50 mL disposable pipets
- 0.5-mL and 1.0-mL micro pipets
- micro pipet tips
- NIST traceable reference standard for target analyte
- HDPE containers

  NaOH for preservation and pH adjustment where applicable
- HCl for pH adjustment where applicable
- pH meter
- personal protective equipment.

3.2 Field Supplies

Battelle will provide the following supplies needed for the collection of field samples:

- ASTM type II water
- 125-mL, 500-mL, 1-L, and 8-L HDPE containers
- 1-mL micro pipet
- 1-mL micro pipet tips
- 10-mL and 50 mL disposable pipets
- HDPE volumetric flasks of various volumes
- coolers and blue ice packs for sample storage
- thermometer
- lead carbonate
- potassium-iodide starch paper
- lead acetate paper
- pH meter
- ascorbic acid
- sodium hydroxide for preservation and pH adjustment where applicable
- HCl for pH adjustment where applicable
- personal protective equipment.

3.3 Reference Instrument

The reference method for analysis of cyanide will be performed on an instrument to be determined as soon as the reference lab is selected. It will be added to the Test/QA plan in the form of an amendment.

4.0 PROCEDURES

4.1 Test Sample Preparation and Storage

QC and PT samples will be prepared from commercially available NIST traceable standard material. The standard will be dissolved and diluted to appropriate concentrations using ASTM Type II water in Class A volumetric glassware. The QC and PT samples will be prepared at start of testing, preserved with NaOH and stored at 4 EC for a maximum of 30 days.

Surface and drinking water samples will be collected from the sources indicated in Section 2.3.3, and will be stored in HDPE containers. Because free chlorine will degrade cyanide during storage, at the time of sampling, all of the samples will be tested for free chlorine with potassium iodide starch (KI) paper. The presence of chlorine is indicated by the KI paper changing to a bright blue color. If chlorine is present, ascorbic acid will be added a few crystals at a time until there is no further color change on the KI paper. Analysis and shipment of the samples to the reference laboratory will then proceed as previously described. For the residential tap water samples, sample analysis will be performed at the time of collection by the analyzers being verified. The rest of the surface and drinking water samples and all of the samples to be analyzed by the reference method will be stored until analysis at 4EC and preserved with sodium hydroxide at a pH of greater than 12. The reference analyses will be performed within 14 days of collection or the field sampling will be repeated.

4.2 Sample Identification

Aliquots to be analyzed will be drawn from the prepared standard solutions or from source and drinking water samples and placed in uniquely identified sample containers for subsequent analysis. The sample containers will be identified by a unique identification (ID) number. A master log of the samples and sample ID numbers for each analyzer will be kept by

Battelle. The ID number, date, person collecting, sample location, and time of collection will be recorded on a chain-of-custody form for all field samples.

4.3 Sample Analysis

4.3.1 Reference Method

The reference instrument will be operated according to the recommended procedures in the instruction manual, and samples will be analyzed according to EPA Method 335.1, Cyanides, Amenable to Chlorination".

Results from the reference analyses will be recorded electronically and compiled by the laboratory performing the analyses into a report format, including the sample ID and the analyte concentration for each sample.

4.3.2 Analyzers Undergoing Verification

Each vendor will be required to provide two units of their portable cyanide analyzer. Each unit will be subjected to the test procedure independently, and separate verification results will be reported for each unit. Those results will then be intercompared to assess unit-to-unit reproducibility. Each of the analyzers being verified will be used to analyze the full set of samples. As shown in Appendix A, the sample set will include replicates of each of the PT, QC, and drinking and surface water samples. Analysis of the complete set of samples will be performed twice for each of the test kit analyzers, once by a non-technical staff member of Battelle, and once by a technical staff member using the same sample aliquot. Because the ion selective electrode analyzers are designed for only the technical user, only a technical operator will perform the analyses for those analyzers. For both types of analyzers, the analyses will be performed according to the manufacturer's recommended procedures as described in the user's

instructions or manual, or during training provided to the Battelle staff. Similarly, calibration and maintenance of the analyzers will be performed as specified by the manufacturer.

Results from the analyzers being verified will be recorded manually by the operator on appropriate data sheets. In addition to the analytical results, the data sheets will include records of the time required for sample analysis and operator observations concerning the use of the analyzer (i.e., frequency of calibration, ease of use, maintenance, etc.).

4.4 Schedule

The verification test described here will take place throughout January 2003 at Battelle's laboratories in Columbus, Ohio and nearby sampling locations. The same samples analyzed by the portable cyanide analyzers undergoing testing will be analyzed by the reference method. All analyzers of the same type being tested will be challenged with the same set of samples. Separate aliquots will be drawn from a single sample for each type of technology. No direct comparison will be made between the results from different analyzers; however, it is to the benefit of potential users of the analyzers that test conditions be as similar as possible.

It will be necessary for participating vendors to provide their analyzers to Battelle by a specified date so project staff may become familiar with operating the units before testing begins. This period will also be used to clarify any questions about the analyzer's operation or maintenance. Vendor staff may choose to be present for this familiarization stage and/or provide training in operating the analyzers either in person or by teleconference. During the verification test, the vendor is encouraged to participate by providing a representative to serve as the technical operator. However, Battelle technical staff will be available to be trained in the operation of the vendor analyzer so the vendor representative does not have to be present for the duration of testing. Battelle will provide non-technical staff to perform the non-technical operator portion of the test kit verification test. Analyzers and associated equipment (if not consumables) will be returned to the vendors at the completion of testing.

5.0 DATA HANDLING AND REPORTING

5.1 Data Acquisition and Review

A variety of data will be acquired and recorded electronically or manually by Battelle staff in this verification test. Operation, maintenance, and results from the analyzers being verified and sampling procedures, will generally be documented on data sheets or in laboratory record books. Results from the reference instruments will be compiled in electronic format.

Records received by or generated by any Battelle staff during the verification test will be reviewed by a more senior Battelle staff member within two weeks after receipt or generation, before these records are used to calculate, evaluate, or report verification results. These records may include electronic records; laboratory record books; sampling records from the field test; or equipment calibration records. The review will be documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy will then be returned to the Battelle staff member who received, generated, or will be storing the record.

In addition, data calculations performed by Battelle will be spot-checked by a more senior Battelle technical staff to ensure that calculations are performed correctly. Calculations to be checked include reference analysis results and statistical calculations described in this test/QA plan.

The data obtained from this verification test will be compiled and reported independently for each analyzer being verified. No intercomparison of the results from one vendor's technology to another's will be made. However, intercomparisons will be made between the results for duplicate analyzers from each vendor.

5.2 Statistical Calculations

5.2.1 Accuracy

Accuracy of the analyzers being verified will be assessed relative to the results obtained from the reference analyses. Samples will be analyzed by both the reference method and the analyzers being verified. The results for each set of analyses will be averaged, and the accuracy will be expressed in terms of a relative average bias (B) as calculated from the following equation:

$$B = \frac{\overline{d}}{\overline{C_R}} \times 100 \qquad (2)$$

where $\overline{d}$ is the average difference between the readings from the analyzer being verified and those from the reference method, and $\overline{C_R}$ is the average of the reference measurements.

Accuracy will be assessed independently for each analyzer to determine inter-unit reproducibility. Additionally, the results will be analyzed independently for the readings obtained from the two operators to determine if significant operator bias exists.

5.2.2 Precision

The standard deviation (S) of the results for the replicate samples will be calculated and used as a measure of analyzer precision at each concentration.

$$S = \left[\frac{1}{n-1} \sum_{k=1}^{n} \left(C_k - \overline{C} \right)^2 \right]^{1/2} \qquad (3)$$

where n is the number of replicate samples, C_k is the concentration measured for the k^{th} sample, and $\overline{C}$ is the average concentration of the replicate samples. The analyzer precision at each concentration will be reported in terms of the relative standard deviation (RSD), e.g.,

$$RSD = \left| \frac{S}{\overline{C}} \right| \times 100 \quad (4)$$

5.2.3 Linearity

Linearity will be assessed by linear regression with the analyte concentration measured by the reference method as independent variable, and the reading from the analyzer being verified as dependent variable. Linearity will be expressed in terms of the slope, intercept, and the coefficient of determination (r^2).

5.2.4 Method Detection Limit

The method detection limit (MDL) for each analyzer will be assessed from the seven replicate analyses of a fortified sample with an analyte concentration of five times the vendor's estimated detection limit (see Tables A-1 and A-2 in Appendix A). The MDL will be calculated from the following equation:

$$MDL = t \times S \quad (5)$$

where *t* is the Student's value for a 99% confidence level, and S is the standard deviation of the replicate samples. The MDL values for the two units of each analyzer will be reported as separate results.

5.2.5 Operator Bias

To assess operator bias for each test kit analyzer, the results obtained from each operator will be compiled independently and subsequently compared. The existence of statistically significant operator bias will be assessed through a *t*-test of the data.

5.2.6 Inter-Unit Reproducibility

The results obtained from two identical units of each analyzer will be compiled independently for each analyzer and for each operator, and compared to assess inter-unit reproducibility. The results will be interpreted using a *t*-test to assess if significant differences exist between the units tested.

5.2.7 Field Portability

The results obtained from the measurements made on drinking water samples in the laboratory and field setting will be compiled independently for each analyzer and for each operator, and compared to assess the accuracy of the measurements under the different analysis conditions. The results will be interpreted using a *t*-test to assess if significant differences exist between the location of testing.

5.2.8 Lethal or Near-Lethal Dose Response

Because the analyzers are not designed to quantitatively measure extremely high concentration water samples that are near-lethal or lethal of consumed, the operators and test coordinator will make qualitative observations of their operation while analyzing such samples.

Observations of unusual operational characteristics (rate of color change, unusually intense color, unique digital readout, etc.) will be documented and reported.

5.3 Data Review

Records generated during the verification test by any Battelle staff be reviewed by a more senior Battelle staff member within two weeks of generation, before these records are used to calculate, evaluate, or report verification results. Table 1 summarizes the types of data to be recorded. These records may include laboratory record books or reference method analytical results. Battelle, contractor, and/or vendor staff will be consulted as needed to clarify any issues about the data records. The review will be documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy will then be returned to the Battelle staff member who generated or who will be storing the record.

5.4 Reporting

The data obtained in the verification test will be compiled separately for each vendor's analyzer, and the statistical evaluations described in Section 4 will be applied to each data set without reference to any other. At no time will data from different vendor's analyzers be intercompared or ranked. Following completion of the statistical evaluations, a draft verification report will be prepared for each vendor's analyzer, stating the verification test procedures and documenting the performance observed. The draft verification reports will each be submitted to the respective vendors for review and comment. Battelle will consider the comments provided by each vendor when revising the verification reports, but does not guarantee that revisions made to the final verification reports will reflect those comments. After vendor review, the revised reports will be submitted to EPA and AMS Center stakeholders for peer review. The reports will

then be revised again to address the peer review comments and submitted for final EPA approval.

Table 1. Summary of Data Recording Process for the Verification Test

Data to be Recorded	Responsible Party	Where Recorded	How often Recorded	Disposition of data[a]
Dates, times of test events	Battelle	Laboratory record books	Start/end of test, and at each change of a test parameter.	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Test parameters (meteorological conditions, analyte concentrations, location, etc.)	Battelle	Laboratory record books	When set or changed, or as needed to document stability.	Used to organize/check test results, manually incorporated in data spreadsheets as necessary.
Reference method sampling data	Battelle	Laboratory record books	At least at the time of sampling	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Reference method sample analysis, chain of custody, and results	Contracted laboratory	Laboratory record books, data sheets, or data acquisition system, as appropriate	Throughout sample handling and analysis process	Transferred to spreadsheets/agreed upon report

(a) All activities subsequent to data recording are carried out by Battelle.

In parallel with preparation of the verification reports will be preparation of the verification statement for each analyzer. The verification statement is a two- to three-page summary of the technology, the test procedures, and the test results. Each draft verification statement will be submitted to the respective vendor for review, and then will follow the same revision and EPA review process as the reports. Upon approval by EPA, each verification statement will be signed by a senior manager of Battelle and by an EPA laboratory director. Battelle will reserve the right to post the final verification reports and statements on the ETV website (http://www.epa.gov/etv). Original signed verification statements will be provided to the respective vendors for use in marketing their products.

6.0 QUALITY ASSURANCE /QUALITY CONTROL

The QA/QC activities associated with this verification test will focus primarily on reference analysis, sample preparation and handling, and data recording and analysis. An independent audit covering each of these areas will be performed by the Battelle Quality Manager to ensure the quality of the verification test.

6.1 QC of Reference Method

Analysis of QC samples throughout the verification test will be used to document the performance of the reference method. RB samples will be analyzed to ensure that no sources of contamination are present. If the analysis of an RB sample indicates a concentration above the MDL for the reference instrument, contamination will be suspected. Any contamination source(s) will be corrected, and proper blank readings will be achieved, before proceeding with the verification test.

The accuracy of the reference method will be verified before the beginning and after the conclusion of each testing day. The instrument to be used for reference (see Section 3.3) will be initially calibrated according to the procedures specified in the reference method. The instrument calibration will be verified using an appropriate QCS (included as part of reference laboratory's SOP). If the QCS analysis differs by more than 25% from the true value of the standard, corrective action will be taken before the analysis of more samples. LFM samples will be analyzed to assess if matrix effects influence the results of the reference method. The percent recovery (R) of the spiked solution will be calculated from the following equation:

$$R = \frac{C_s - C}{s} \times 100 \qquad (6)$$

where C_s is the analyzed concentration of the spiked sample, C is the analyzed concentration of the unspiked sample, and s is the concentration equivalent of the cyanide spike. If the percent recovery of an LRM falls outside the range from 75-125%, a matrix effect will be suspected.

6.2 Audits

6.2.1 Performance Evaluation Audit

A performance evaluation (PE) audit will be conducted to assess the quality of the reference measurements made in this verification test. A performance evaluation audit involves challenging the instruments used for reference method with standards that are independent of those used to calibrate the instruments for the test. For the PE audit, an independent standard will be obtained from a vendor that is different from the one that supplied the QC standards. This comparison of the QC and performance evaluation standards will be done once during the verification test. Agreement of the standards within 25% is required for the measurements to be considered as acceptable. Failure to achieve this agreement will trigger a repeat of the performance evaluation comparison. Failure in the second comparison requires obtaining another set of standards, and repeating the performance audit.

6.2.2 Technical Systems Audit

The Battelle Quality Manager will conduct a technical systems audit at least once during the course of the verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with this test/QA plan and the AMS Center QMP[1], and that all procedures described in this test/QA plan are being followed. This audit will review the

reference standards and methods used, compare actual test procedures to those specified in this test/QA plan, and review data acquisition and handling procedures. An independent technical systems audit may also be performed by EPA Quality Management staff during the verification test, at EPA's discretion.

As referred to in Section 1.3.4, Battelle will submit various solutions with known concentrations of cyanide to prospective commercial laboratories to test their ability to accurately measure cyanide. After the reference lab reports the cyanide concentrations in those solutions to within 25% of the known concentration, the Battelle Quality Manager will conduct an audit of the reference laboratory's quality documents. If there are areas of concern with the quality documents, the commercial laboratory will be notified, and if they are willing to adapt their procedures, the laboratory will still be used. If not, another laboratory will be selected and their performance will be verified in a similar manner.

6.2.3 Audit of Data Quality

At least 10% percent of the data generated during the verification test will be audited during the verification test. Battelle's Quality Manager will trace the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit will be checked.

6.3 QA/QC Reporting

Each assessment and audit will be documented in accordance with Section 3.3.4 of the QMP for the AMS Center. The results of the technical systems audit will be sent to the EPA. Assessment reports will include the following:

- Identification of any adverse findings or potential problems.
- Response to adverse findings or potential problems.
- Recommendations for resolving problems.
- Confirmation that solutions have been implemented and are effective.
- Citation of any noteworthy practices that may be of use to others.

6.4 Corrective Action

The Battelle or EPA Quality Managers during the course of any assessment or audit will identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken.

7.0 HEALTH AND SAFETY

7.1 Handling of Sodium Hydroxide and Potassium Cyanide

7.1.1 Laboratory Standard/Performance Test Sample Preparation

All handling of solid and highly concentrated aqueous solutions of potassium cyanide and sodium hydroxide will be done inside of a laboratory hood with hood sash set to the lowest height that still allows for safe manipulation of materials. The following guidelines should be adhered to:

- Personal protective equipment shall include safety glasses with side shields, a laboratory coat and nitrile lab gloves. Gloves shall be immediately changed if they become contaminated. (The same gloves can be used for sodium hydroxide)
- All contaminated waste shall be handled as hazardous waste and sent out through Battelle Waste Operations.

7.1.2 Field and Laboratory Handling During Verification Testing

Field handling of the cyanide and sodium hydroxide solutions will be accomplished by taking the following precautions:

- All containers shall be stored and transported in double containment.
- Safety goggles, nitrile gloves with long cuffs, and a chemical resistant disposable lab coat shall be worn when handling either chemical. Gloves shall be immediately changed if they become contaminated.

8.0 REFERENCES

1. "Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center", Version 3.0, Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, December 2001.

2. U.S. EPA Method 335.1, Cyanides, Amenable to Chlorination, 1974.

APPENDIX A

SUMMARY OF TEST SAMPLES FOR PORTABLE CYANIDE ANALYZERS

Table A-1. Summary of the Colorimetric Test Kit Verification Test Samples[a] for Cyanide

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	RB [b]	~ 0	10% of all
	LFM [b]	0.2 mg/L[c]	4 per water source
	QCS [b]	0.2 mg/L	10% of all
Performance Test	For the determination of detection limit	Five times the manufacturer's estimated detection limit	7
	Cyanide	0.03 mg/L	4
	Cyanide	0.1 mg/L	4
	Cyanide	0.2 mg/L	4
	Cyanide	0.4 mg/L	4
	Cyanide	0.8 mg/L	4
Lethal / Near-Lethal Samples	Cyanide	50 mg/L	4
	Cyanide	100 mg/L	4
	Cyanide	250 mg/L	4
Drinking and Surface Water	Residence with Columbus water	Unknown	3 or 12[d]
		0.2 mg/L LFM	12
	Residence with well water	Unknown	3 or 12
		0.2 mg/L LFM	12
	Alum Creek Reservoir	Unknown	1 or 4
		0.2 mg/L LFM	4

	Olentangy River	Unknown	1 or 4
		0.2 mg/L LFM	4
	Northwestern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4
	Southwestern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4
	Midwestern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4
	Southeastern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4
	Northeastern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4

[a] Listing is for clarity; samples will be analyzed in randomized order for the verification testing.
[b] See Section 2.3.1 for descriptions of these samples.
[c] MCL for cyanide.
[d] If the initial unspiked aliquot gives a non-detectable response, no further unspiked aliquots will be measured. However, if there is a detectable response in the initial aliquot, three additional aliquots will be analyzed for a total of four analyses for each water sample. Three water samples are analyzed at each residence (3 or 12 total samples) and one water sample for the other sample types (1 or 4 total samples).

Table A-2. Summary of the Ion Selective Electrode Verification Test Samples[a] for Cyanide

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	RB [b]	~ 0	10% of all
	LFM [b]	0.2 mg/L[c]	4 per water source
	QCS [b]	0.2 mg/L	10% of all
Performance Test	For the determination of detection limit	Five times the manufacturer's estimated detection limit	7
	Cyanide	0.03 mg/L	4
	Cyanide	0.1 mg/L	4
	Cyanide	0.2 mg/L	4
	Cyanide	0.4 mg/L	4
	Cyanide	1 mg/L	4
	Cyanide	5 mg/L	4
	Cyanide	15 mg/L	4
	Cyanide	25 mg/L	4
Drinking and Surface Water	Residence with Columbus water	Unknown	3 or 12[d]
		0.2 mg/L LFM	12
	Residence with well water	Unknown	3 or 12
		0.2 mg/L LFM	12
	Alum Creek Reservoir	Unknown	1 or 4
		0.2 mg/L LFM	4
	Olentangy River	Unknown	1 or 4
		0.2 mg/L LFM	4
	Northwestern U.S.	Unknown	1 or 4

		0.2 mg/L LFM	4
	Southwestern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4
	Midwestern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4
	Southeastern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4
	Northeastern U.S.	Unknown	1 or 4
		0.2 mg/L LFM	4

[a] Listing is for clarity; samples will be analyzed in randomized order for the verification testing.
[b] See Section 2.3.1 for descriptions of these samples.
[c] MCL for cyanide.
[d] If the initial unspiked aliquot gives a non-detectable response, no further unspiked aliquots will be measured. However, if there is a detectable response in the initial aliquot, three additional aliquots will be analyzed for a total of four analyses for each water sample. Three water samples are analyzed at each residence (3 or 12 total samples) and one water sample for the other sample types (1 or 4 total samples).